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HEAT STABLE POLYMERS:
POLYPHENYLENE AND
OTHER AROMATIC POLYMERS

Final Report

J. K. Stille

January 1974-December 1976

U.S. Army Research Office

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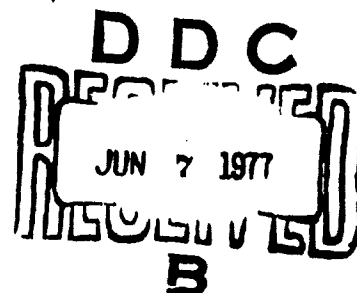
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of polyphenylenes were synthesized by the reaction of 5,5'- m- and p-phenylenebis-2-pyrones with m- and p-diethynylbenzene increasing the ratio of m- to p-phenylene links in the chain increases the solubility and decreases the crystalline transition temperature. Model reactions on 4- and 6-phenyl-2-pyrones show that this monomer type is unsuitable for the syntheses of polyphenylenes with higher portions of m-catenation. The 4- and 6-phenyl-2-pyrones have been used, however, to prepare polyimides by reaction with a series of bismaleimides. Model reactions of 3,4-diphenyl-		

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20. ABSTRACT (continued)

thiophenedioxide also demonstrate that this monomer type is unsuitable as a diene in 4+2 cycloaddition polymerizations.

Amorphous polyaramides have been obtained by the polymerization of aromatic diamines with 4,4'-[sulfonylbis(p-phenyleneoxy)]dibenzoic chloride. Triphenylphosphite prepared in situ has been shown to be an effective catalyst for the preparation of polyaramides from the free acid and amine.

Polyquinolines can be synthesized by a polymerization reaction that allows a variety of structural modification, resulting in range of chain stiffness that can be altered from a relatively flexible polymer with a low glass transition temperature to a rod-like molecule with a high glass transition temperature. The polymerization reaction is acid catalyzed, but is carried out most effectively by a new polymerization agent, dicresyl phosphate. The polymers are soluble in common organic solvents, such that fibers can be dry-spun and transparent fibers can be cast from solution. Excellent thermal stability is observed for these materials.

Thermal curing of both phenylated polyphenylenes and polyquinolines has been accomplished by employing the cyclotrimerization of aryl cyanates. Biscyanatoprepolymer were synthesized by the reaction of cyanogen bromide with the corresponding hydroxy end-capped oligomers.

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INTRODUCTION

Along with the developments in the aerospace industry and other advanced technology came an increased demand for new materials that could withstand severe environmental conditions. The greatest emphasis has been placed on the development of materials capable of withstanding temperatures up to 350°C for periods up to 400 hr, or temperatures up to 530°C for 80 hr. These demands for thermal stability might appear to be outside the capabilities of an organic material, yet there is good evidence that specially synthesized organic polymers, particularly those that are composed entirely of aromatic rings or aromatic rings linked by stable connecting groups, would serve the necessary functions of a structural material and at the same time be thermally stable.

Step-growth polymerizations offer the more attractive means of synthesis of such stable rigid chain polymers, particularly those polymerizations that produce aromatic rings as the polymer-forming reaction. Linear rigid chain macromolecules generally exhibit greater mechanical strength and higher phase transition temperatures than the more flexible chain polymers. Most of the polymers with highly rigid recurring units in the chain, however, are either crystalline, or have high melting (softening) temperatures and are insoluble in suitable solvents as a result of ring (particularly aromatic ring), spiro, or ladder structures in the main chain. Polymers which owe their rigidity to a high percentage of aromatic units offer unique opportunities for studying the relationship between the molecular motion of chains and their effect on the thermal and solution properties. In the absence of appreciable intramolecular chain attraction--such as hydrogen bonding--the internal rotations of chain segments are greatly restricted and can be correlated with phase transitions, relaxations and conformation in solution.

A polymer with a high use-temperature is defined by two variables of thermal performance: 1) A threshold temperature at which the polymer loses

its mechanical strength under an external applied load of specified magnitude.

2) A threshold temperature corresponding to the occurrence of chemical changes in the structure of the polymer accompanied by corresponding changes in properties. The first variable requires a material with a high glass transition temperature, a high crystalline temperature combined with a relatively high degree of crystallinity, or a three dimensional network structure. In order to achieve melt processability, the synthesis of an uncross-linked material with relatively low transition temperatures is necessary. Subsequently these transition temperatures can be raised by some chemical means after processing to give a more rigid chain or a three-dimensional network structure. An alternate approach to this problem is to process the polymer in the amorphous state in which a moderately high glass transition temperature (e.g., 250-350°C) is obtained and then develop crystallinity during processing or subsequent annealing to raise the use temperature (e.g., $T_m = 450-550^\circ\text{C}$) to the limit of thermal performance as defined by the second variable.

POLYPHENYLENES

Background

The 4 + 2 cycloaddition reaction of diacetylenes with bisdiene monomers containing two cyclopentadienone groups has been demonstrated to afford high molecular weight polyphenylenes.¹⁻¹⁰ In the polymerization reaction of a biscyclopentadienone, a new benzene ring containing pendent phenyl groups is formed with the loss of carbon monoxide. The unusually high solubility of these polyphenylenes can be attributed to either pendent phenyl substitution or to the presence of some meta-catenation which can occur in the newly formed benzene ring as a result of the orientation in the cycloaddition reaction. Both could be considered to render the polymer amorphous and thus account for the good solubility.

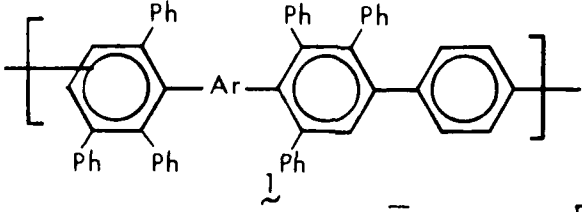

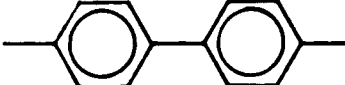
Under the polymerization conditions, it has been shown⁹ that approximately

half of the phenylated phenylene rings formed as a result of the Diels-Alder reaction provide meta-catenation. Light scattering measurements in fractionated polymer 1a give a mean-square radius of gyration which supports this degree of meta-catenation. The magnitude of the second virial coefficient is very small and indicates that the expansion coefficient is nearly unity. Furthermore, there is very little dependency of the intrinsic viscosity on the solvent.

A comparison (Table 1) of polymers (1a, 1b) containing different degrees of p- vs m-catenation shows that an increased amount of p-catenation increases the solution viscosity as a result of greater rod like character.

TABLE 1

Intrinsic Viscosities of 1

		
Polymer <u>1</u>	\bar{M}_n	$[\eta]$ (dl/g)
<u>1a</u> . Ar = 	44,000	0.68
<u>1b</u> . Ar = 	30,000	1.0

These phenylated polyphenylenes obtained from the 1,4-cycloaddition reaction of biscyclopentadienones with bisacetylenes have properties which are quite different from those of the unsubstituted polyphenylenes prepared by other methods⁸. The phenylated polyphenylene in which the phenylated rings have a 1:1 para- to meta-catenation ratio, and have number-average molecular weights of 20,000-100,000 are light yellow, amorphous, and

completely soluble in common organic solvents (benzene, chloroform, tetrahydrofuran, etc.) in concentrations up to ten weight percent. By contrast, those polyphenylenes prepared either from benzene by a Friedel-Crafts reaction under oxidative conditions or by the 1,4-polymerization of 1,3-cyclohexadiene followed by dehydrogenation are brown to black, crystalline and insoluble. Because of these differences in physical properties of the two kinds of polyphenylenes, the synthesis of an unphenylated polyphenylene by a Diels-Alder route was of particular interest.

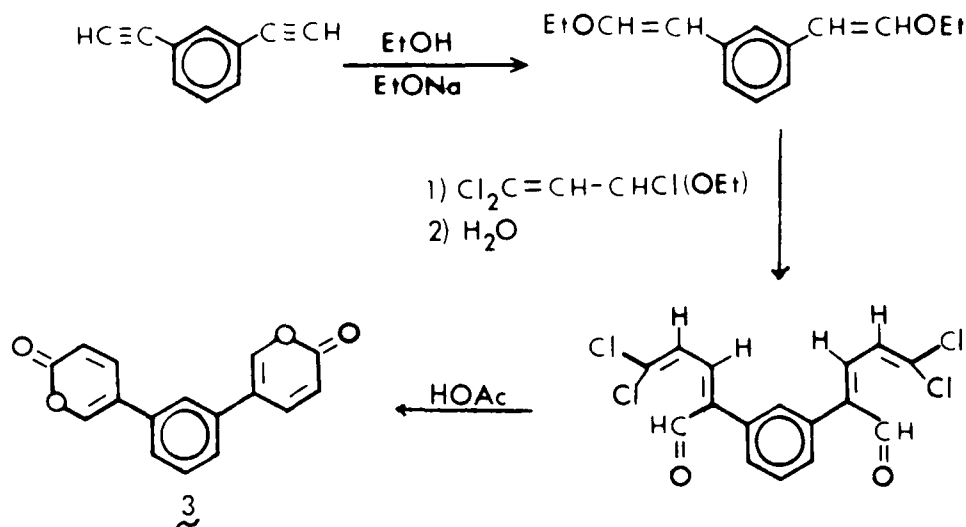
Unsubstituted Polyphenylenes

The reaction of 5,5'-p-phenylenebis-2-pyrone (2) with both m- and p-diethynyl benzene afforded unsubstituted polyphenylenes 4^{11,12} and 5. The newly formed benzene ring obtained from the 4 + 2 cycloaddition followed by the loss of carbon dioxide is >95% para in this case. Thus unsubstituted polyphenylenes with known degrees of p- and m-catenation are obtained (Fig 1).

Poly(p-phenylene) (4) is a yellow, crystalline, insoluble polymer of unknown molecular weight. It precipitates as a powder in the course of the polymerization reaction which is run at 230°. Polyphenylene 5, which contains a m-phenylene group every fourth phenylene unit, is also yellow, crystalline, and insoluble. This polymer, however, deposits as a film on the walls of the ampoule during the course of the polymerization reaction; some powder precipitates also. Possibly the m-phenylene unit provides enough flexibility in the polymer chain to give added solubility, allowing the polymer to achieve a higher molecular weight before separating, and thereby producing a coherent film. Polyphenylene 5 was also synthesized by the

reaction of *p*-diethynylbenzene with 5,5'-*m*-phenylenebis-2-pyrone (3) and the synthesis of this pyrone allowed the preparation of a polyphenylene 6, containing alternate *p*- and *m*-phenylene rings.

Polymerizations with 5,5'-*m*-phenylene-2-pyrone. The synthesis of 5,5'-*m*-phenylenebis-2-pyrone was achieved in a manner analogous to that previously reported for the corresponding *p*-isomer¹². The synthesis of *cis*, *cis*-3,3'-diethoxy-1,3-divinylbenzene was accomplished by the base catalyzed addition of ethanol to *m*-diethynylbenzene. The reaction of this vinyl ether with trichloropropenyl ethyl ether afforded a condensation product which was hydrolyzed to yield 1,3-bis-(5,5'-dichloropenta-2,4-dienal-2-)benzene. Cyclization to the pyrone was accomplished with refluxing acetic acid.



The polycondensation of 2 with *m*-diethynylbenzene as well as that of 3 with *p*-diethynylbenzene were carried out under a variety of reaction conditions to give the same polyphenylene (5).

As in the preparation of poly(*p*-phenylene), the polymerizations were

performed in 1,2-dichloroethane and in 1,2,4-trichlorobenzene at high temperatures (230°C). However, incomplete solubility of the meta bis pyrone 3 was observed and therefore the polymerization reaction was not a homogeneous system. Two other solvents were found to completely dissolve this reactant, even at room temperature: 1,1,2,2-tetrachloroethane and N-methyl pyrrolidinone. Since the tetrachloroethane readily decomposes at the polymerization temperature and cannot be used at its boiling temperature (146°C) to produce a high molecular weight polymer (intense π carbonyl absorption), the N-methyl pyrrolidinone was found to be the best solvent in which to carry out the polymerization. In addition, it was also observed that the polymer prepared in this solvent in nearly quantitative yield no longer shows a pyrone carbonyl absorption.

In the preparation of polymers 5 in various solvents and 6 in N-methyl pyrrolidinone, the formation of a dark brown film coating the walls of the glass polymerization tube was observed. This film, which was electrostatic, was insoluble and showed essentially no absorption corresponding to the functional groups in the monomers. The fact that a film was formed during the polymerization presumes the presence of a polymer with a higher molecular weight than that observed for the poly(p-phenylene).¹² The rest of the reaction product consisted of a yellow-brown precipitate. The ratio of yields between film and powder varied considerably with the nature of the solvent and the polymerization temperature but, in all cases, the overall yields are quantitative.

When prepared in other solvents, polymer 6 was a yellow-brown powder. The 1,2,4-trichlorobenzene soluble portion (45%) of polymer 6, prepared in this same solvent, had an intrinsic viscosity of 0.09 dl/g. However, no additional information about the chain length could be obtained from the the infra-red study.

The infra-red spectrum of polymer 5 showed two strong absorptions at 785 and 820 cm^{-1} characteristic of the C-H out of plane deformations of the meta and para phenylene moiety respectively. The same observations were made at 785 and 840 cm^{-1} for polymer 6. It is interesting to compare the frequency for the C-H out of plane deformation of the para phenylene groups with the poly(p-phenylene) and observe the shift to higher wavenumbers with decreasing degree of para phenylation.^{9,14,15} However, estimation of the amount of m- versus p-catenation in the polymer by comparing the infra-red spectrum of the polymer with that of standard mixtures of m- and p-terphenyl was not possible because the bands broaden and shift in the polymer spectrum causing an overlap of the CH deformation bands.

A very strong absorption near 895 cm^{-1} due to the CH deformation of the isolated hydrogen in meta-substituted benzene was also observed for these new polyphenylenes.

The λ_{max} (refl.) of the polyphenylenes containing some degree of meta catenation were found in the range of 304 to 325 nm. Since the presence of meta catenation impedes the conjugation of more than four phenylene groups (polymer 5) or three phenylene units (polymer 6),¹⁶ it was not possible to compare these values with those of the poly(p-phenylene)¹² and thereby obtain additional information about the molecular weight of these polymers using Kuhn's root law.¹⁷

All these polymers were found to be highly crystalline showing reproducible d spacings at 4.7, 3.85 and 3.2 Å for polymer 5 and at 4.8, 4.3, 3.8 and 3.25 Å for polymer 6. A film of polymer 5 showed an additional diffraction at 7.5 Å.

As expected, the new polyphenylenes showed excellent thermal stability. The TGA of a film of polymer 5 showed breaks at 500°C in nitrogen with

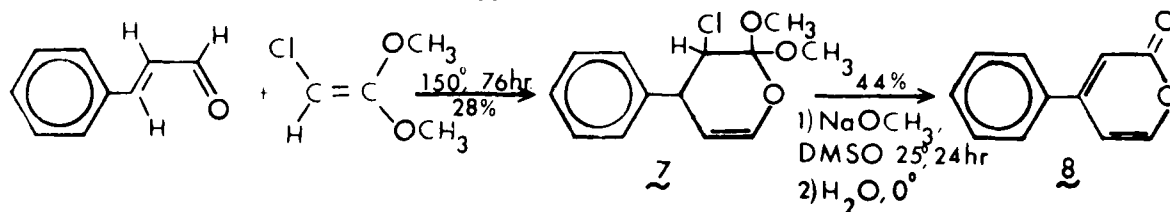
a weight loss of 10% at 640°C and 50% at 800°C and complete decomposition at 485°C in air. The TGA of the powder sample of polymer 5 prepared in a better yield in 1,2,4-trichlorobenzene, showed a break at 580°C in nitrogen with a weight loss of 10% at 620°C and 22% at 800°C and a break at 480° in air. Polymer 6 with approximately 50% meta catenation showed a break at 575° in nitrogen with a weight loss of 25% at 800°C while complete decomposition occurred at 550° in air.

The effect of p-catenation in these polyphenylenes is evidenced in the crystalline transition temperatures. Poly(p-phenylene) has the highest crystalline transition temperature, evidently above its decomposition temperature. Increasing the portion of m-units lowers T_m . The glass transition temperatures in these highly crystalline materials were observed on amorphous materials prepared by heating samples above T_m and then quenching in liquid nitrogen.

Reactions of 4- and 6-Phenyl Pyrone. Although polyphenylenes containing alternating m- and p-phenylene rings apparently are more soluble than polyphenylenes having fewer m-units in the chain, their low solubility precludes fabrication from solution. To improve the solubility of unsubstituted polyphenylenes to the extent exhibited by the phenylated polyphenylenes, the synthesis of a polymer containing all m-catenation would be desirable. Since molecular orbital calculations showed¹⁸ that the Diels-Alder reaction of either 4-phenyl-2-pyrone or 6-phenyl-2-pyrone with phenylacetylene would yield predominately m-terphenyl, the syntheses of these pyrones was undertaken to study the suitability of these types of dienes in polymerization.

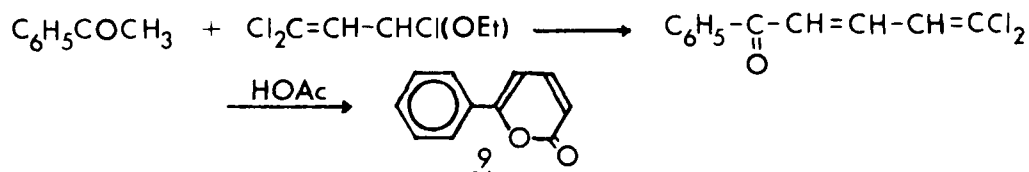
The synthesis of 4-phenyl-2-pyrone has been described.^{19,20} The condensation of cinnamaldehyde with chloroketene dimethylacetal affords 3-chloro-3,4-dihydro-2,2-dimethoxy-4-phenylpyrone (7) which is treated

with sodium ethoxide to afford pyrone 8.



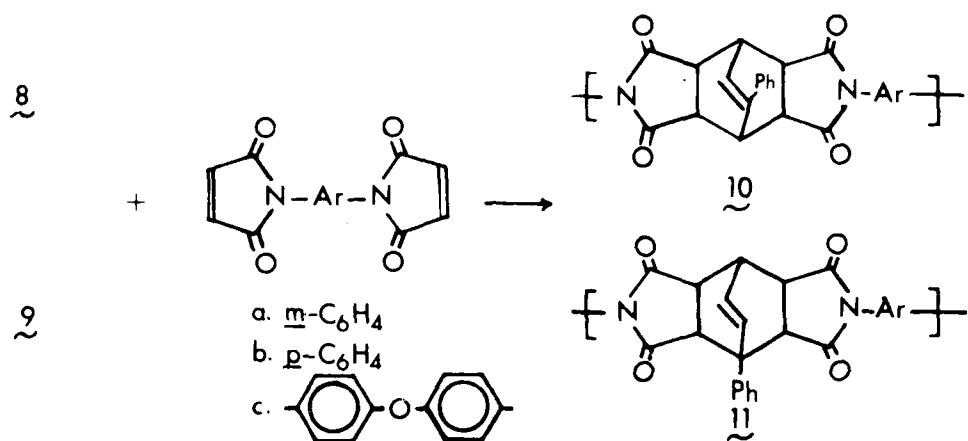
The Diels-Alder reaction of 4-phenyl-2-pyrone (8) with phenyl acetylene gave both *p*- and *m*-terphenyl in a 1:2 ratio. Unfortunately, only a 69% yield was obtained, making this synthesis unsuitable as a polymer forming reaction.

The synthesis of 6-phenylpyrone 9 was accomplished by modification of literature procedures.^{12,21,23} The reaction of acetophenone with 1,1,3-trichloro-3-ethoxypropene afforded 5,5-dichloro-2,4-pentadienophenone, which was cyclized by heating in acetic acid. The model reaction of 9 with phenyl-



acetylene yielded (34%) both *o*- and *m*-terphenyls in a 5.4:1 ratio. A similar direction of addition (5:1) is obtained in the reaction of 4,5,6-triphenylpyrone.²⁴

Polymerization of 4- and 6-Phenylpyrones with Bismaleimides. Since N-substituted maleimides are more reactive dienophiles in 4 + 2 cycloadditions involving α -pyrones, polymerization reactions of 4- and 6-phenylpyrones with a series of bismaleimides were carried out to afford polyimides having the bicyclo[2.2.2]oct-7-ene unit in the chain. In this polymerization, the stoichiometry of diene to dienophile unit is 1:2, since the initial Diels-Alder intermediate adduct loses carbon dioxide to generate a new diene.



These polymers differ from related polyimides²⁵⁻²⁸ in that they have only one substituent (phenyl) in the bicyclooctene segment. The stereochemistry of these reactions (exo-exo vs endo-endo) has not yet been determined. Other work^{29,31} indicates that pyrones substituted in the 6-position give cycloaddition products opposite from that predicted by maximum orbital overlap.

Although optimum polymerization conditions have not yet been determined, polymers having intrinsic viscosities (DMSO, 25°C) of 0.22, 0.49, and 0.50 have been obtained for the polymers 11a-c. Films cast from N-methyl pyrrolidone solutions of polymers 11b and 11c were yellow, transparent, and had glass transition temperatures (Tg's) (differential scanning calorimetry, nitrogen atmosphere) of 325°C and 315°C, respectively. An intense endotherm occurred immediately above the Tg's in both cases, even after isothermally aging at 200°C for forty minutes, which may be due to the cross-linking discussed below. The film of the ether-linked polymer (11c) was considerably tougher than that of the brittle p-phenylene linked polymer (11b). The polymers are soluble in N-methyl pyrrolidone, dimethyl sulfoxide, and dimethyl formamide.

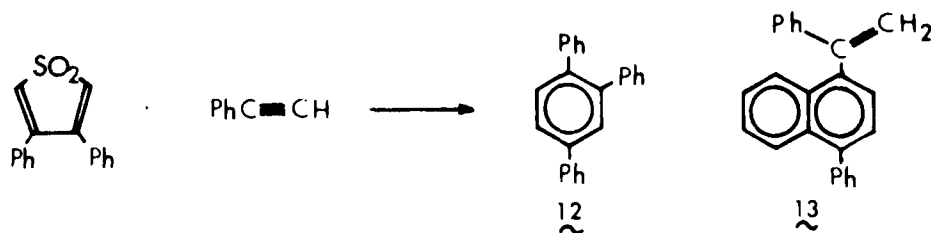
Considerable difficulty was encountered with gelation occurring late

in the polymerization reactions of monomer 9. Possibly this is due to cross-linking by grafting of a terminal 1,3-cyclohexadiene with one of the bridging olefins in the bicyclooctene polymer backbone (11). Gelation has not been a problem in polymerizations employing 5-phenylpyrone (8); a phenylsubstituent on one carbon of the bridging olefin apparently sterically hinders the approach of any diene terminus.

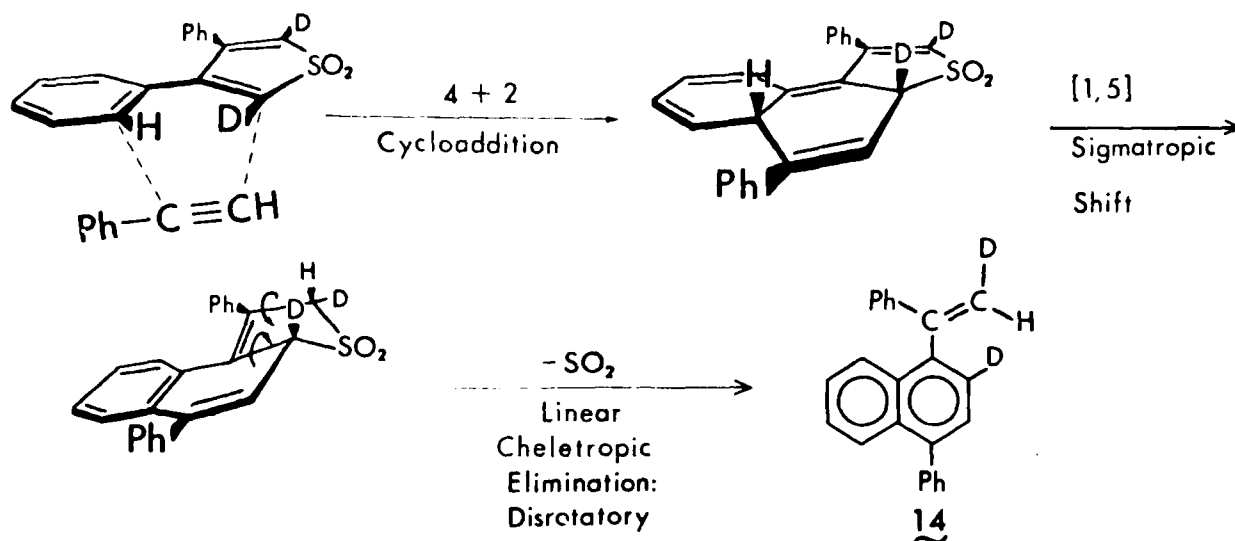
Reaction of 3,4-diphenylthiophene-1,1-dioxide

Because of the reactivity of cyclopentadienones substituted only in the 3- and 4- positions, the use of suitable cyclopentadienone monomers for the synthesis of polymers bearing minimal phenyl substitution is not feasible. Thus, the model reaction of 3,4-diphenylthiophene-1,1-dioxide with phenylacetylene was explored.

The major product of the reaction of 3,4-diphenylthiophene-1,1-dioxide with phenylacetylene was not 1,2,4-triphenylbenzene (12), as expected, but an isomer, 1-phenyl-4-(1-phenylethenyl)naphthalene (13)³¹. The identity of 13 ultimately was established by an independent synthesis.



When 2,5-dideuterio-3,4-diphenylthiophene-1,1-dioxide was employed in this reaction, (E)-3-deuterio-1-phenyl-4-(2-deuterio-1-phenylethenyl)naphthalene) 14 was produced, verifying that the 1-phenylethenyl moiety originated from the thiophene dioxide. The nearly exclusive formation of the E-isomer requires three consecutive concerted orbital symmetry-controlled reactions as shown.³¹



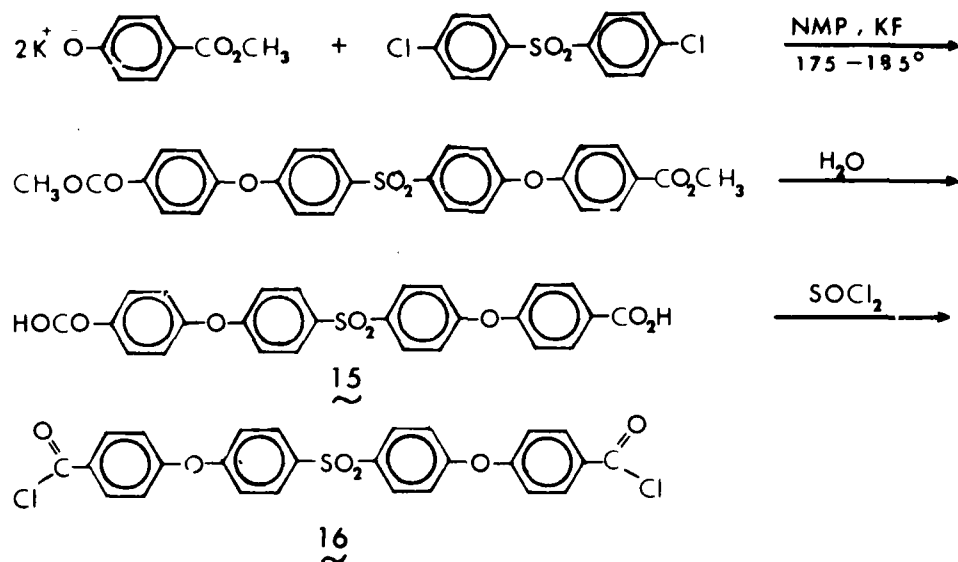
Further exploration of this reaction for the synthesis of polyphenylenes containing minimal phenyl substitution was abandoned.

POLYAMIDES^{32,33}

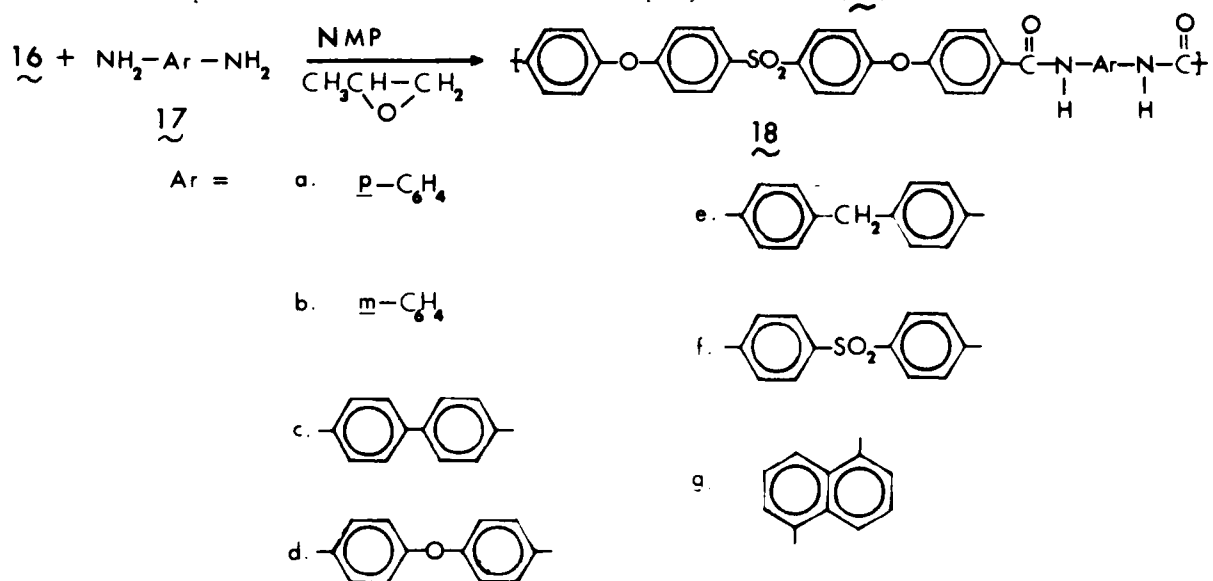
Aromatic polyamides containing aryl ether or aryl sulfone links have increased chain flexibility and lower glass transition temperatures than those of crystalline polyaramides in which these groups are absent. Aromatic polyamides containing both aryl sulfone and aryl ether links between amide groups obtained by the polyamidation reaction of 4,4'-[sulfonylbis(p-phenyleneoxy)]dianiline with isophthaloyl or terephthaloyl chlorides, for example, are amorphous.³⁴ These polyaramides have glass transition temperatures of 230 and 260°, respectively, and show excellent mechanical properties. Polyaramides of this general structure are of interest since they offer the possibility of facile processability, especially by melt techniques; in addition they should possess the superior thermal stability displayed by the crystalline polyaramides.³⁵

The synthesis of 4,4'-[sulfonylbis(p-phenyleneoxy)]dibenzoic acid (15) was accomplished by reaction of the potassium salt of methyl p-oxybenzoate and 4,4'-dichlorodiphenylsulfone, followed by hydrolysis of the resulting

diester. Diacid 15 was converted to the diacid chloride, 4,4'-[sulfonylbis(p-phenyleneoxy)]dibenzoic chloride (16) with thionyl chloride.



The polycondensation reaction of the diacid chloride (16) with various aromatic diamines (17) in N-methylpyrrolidone containing propylene oxide as an acid acceptor^{36,37} afforded a series of polyaramides (18). In the reaction



of 16 with 4,4'-diaminodiphenylether (17d), various acid acceptors (Table 2) were added. Propylene oxide afforded the highest molecular weight polymer as

measured by inherent viscosity.

Polyamides (18a-g) (Table 3), obtained by reaction in NMP in the presence of propylene oxide, were completely soluble in sulfuric acid, DMF and NMP, but only the polymers with more flexible chains were soluble in m-cresol. The polyamides were largely amorphous with glass transition temperatures near 250°C, typical of polyaromatics containing p-phenylene ether and sulfone links. Polyamides prepared from the more rigid diamines, 18a, c, g were partially crystalline.

TABLE 2
POLYCONDENSATION REACTION OF DIACID CHLORIDE 16 WITH
4,4'-DIAMINODIPHENYLETHER (17d)^a

Solvent (25 ml)	Acid Acceptor	η_{inh}^b
NMP	propylene oxide (1.5 ml)	1.96
	CaO (0.190 g)	1.48
	Et ₃ N (2 ml)	1.19
DMAC	-	0.80
	CaO (0.190 g)	0.83
HMPA	-	1.18
	Et ₃ N (2 ml)	1.25

^a Monomer concentration: 0.26 molar (9.7 wt%). Initial reaction temperature = -30°C.

^b In DMF at 25°C.

TABLE 3
POLYAMIDES 18a-g FROM DIACID CHLORIDE 16 AND
AROMATIC DIAMINES 17a-g.

Polyamide 18	η_{inh}^a	Solubility ^c			DSC	T _g ^d		T _m
		DMF or NMP	m-Cresol			TMA		
a	1.18 ^b	s	i		260 ^e	280 ^e		450 ^f
b	0.97	vs	vs		245	255		-
c	1.19 ^b	s	i		-	-		- ^g
d	1.96	vs	s		260	250 255		-
e	0.71	vs	vs		250	255 260		-
f	0.78	vs	s					
g	1.55	vs	s		260 ^e	-		375

^aDMF at 25°C.

^b96% H₂SO₄ at 25°C.

^cvs=very soluble; s=difficulty soluble; i=insoluble.

^dObtained on a du Pont 990 Thermal Analyzer with a differential scanning calorimeter and a 943 Thermomechanical Analyzer.

^eT_g observed only after heating the sample above T_m and quenching in liquid nitrogen.

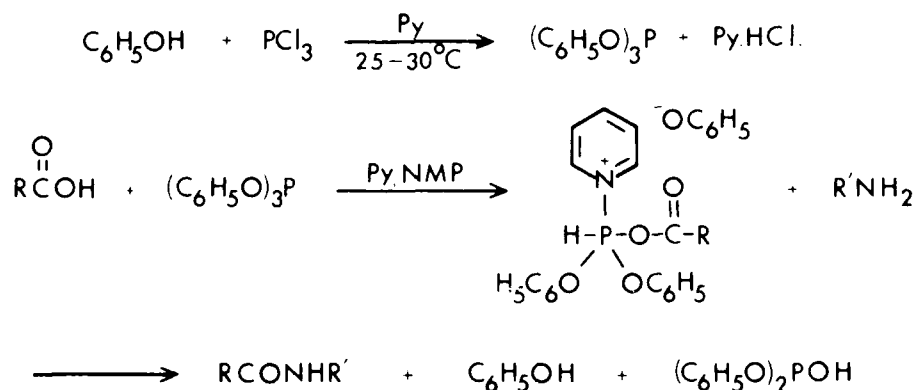
^fT_c = 310°C.

^gUnable to observe T_g due to partial crystallinity. T_m is above T_d (430°C).

The solution polycondensation of terephthaloyl chloride with p-phenylenediamine or the homopolymerization of p-thionylaminobenzoyl chloride, affords high modulus, thermally stable polyamides³⁸. Aromatic polyamides also have been obtained by the direct polycondensation reaction of aromatic dicarboxylic acids with aromatic diamines catalyzed by triphenylphosphite in NMP-pyridine solution containing p-chloride at 100°C.³⁹ Trimellitic anhydride reacts

with 4,4'-diaminodiphenylmethane in the presence of triphenylphosphite at 200-210°C, in NMP to form a polyamide-imide.⁴⁰

Because of the desirability of a direct synthesis of polyaramides from the acid and amine, a polyamidation reaction catalyzed by triphenylphosphite prepared in situ from phenol and phosphorous trichloride in the presence of excess pyridine was developed.³³ The proposed mechanism³⁹ for this polycondensation reaction requires a mixed anhydride.



Since pyridine is not a good solvent for polyaramides, but is necessary for catalyst formation, the polycondensation of p-aminobenzoic acid (p-ABA) depends both on the concentration of monomer and the amount of pyridine. For a 0.4 molar concentration of monomer the necessary minimum amount of pyridine is 20% (1:4 v/v, pyridine/NMP Table 4). Table 5 shows the effect of monomer concentration in this polycondensation reaction; the highest viscosity is obtained at a monomer concentration of 0.40 molar (11%). Optimum conditions for the polycondensation reaction between isophthalic acid and aromatic diamines were obtained under the same conditions but with 50% pyridine (Table 6). In each case the temperature of the reaction was increased slowly from 80-90°C (2 hr) to 100-105°C, where it was held for 4 hr. Temperatures higher than 100-105°C, did not improve the viscosity.

TABLE 4

Effect of Pyridine in the Polycondensation Reaction of p-ABA^a

Pyridine ml(%)	NMP ml	η_{inh}^b
30(60%)	20	1.05
20(40%)	30	1.00
10(20%)	40	1.64
5(10%)	45	1.18

^a Monomer con. 0.4 molar; 4 wt % LiCl.^b H₂SO₄ at 25°C.

TABLE 5

The Effect of Monomer Concentration on the
Polycondensation Reaction of p-ABA^a

Solvent ml	Monomer Concentration mole/l (wt%)	η_{inh}^b
60	0.33 (9)	1.39
50	0.40 (11)	1.64
40	0.50 (14)	1.45

^a NMP/Py = 40/10 (vol), 4 wt % LiCl added.^b H₂SO₄ at 25°C.

TABLE 6

Effect of Pyridine in the Polycondensation Reaction of
Isophthalic Acid with p-Phenylenediamine.^a

Pyridine ml (%)	NMP ml	η_{inh}^b
20 (50%)	20	1.11
15 (37.5%)	25	0.89
10 (25%)	30	0.72

^a Monomer conc = 0.5 molar in NMP-Pyridine with 4 wt % LiCl added.


^b H_2SO_4 at 25°C.

The positive influence of 3-4% lithium chloride in polycondensation reaction for aromatic polyamides is well-known in many cases.^{38,39,41,42} In these reactions, low viscosities were obtained without lithium chloride, since early precipitation of the polymer occurred. Polymers from isophthalic acid and amines 17c and 17g as well as the polymers from terephthalic acid (Table 7) are lower molecular weight, since they precipitated from the reaction solution as a result of their rigid structure.

Thus, polyamidation can be carried out simply by forming triphenylphosphite in situ. It is not necessary to isolate this catalyst since the pyridine hydrochloride by-product apparently does not affect the reaction. The success of this reaction in the synthesis of high molecular weight polymers requires, however, that the polyamides have good solubility in the solvent system.

TABLE 7

Synthesis of Aromatic Polyamides by Means of
Triphenylphosphite Prepared in situ^a

Diamine <u>17</u>	Dicarboxylic Acid	η_{inh}^b
a	isophthalic	1.11
c		0.35
d		0.89
e		0.96
g		0.48
d	terephthalic	0.24
e		0.3
		1.69

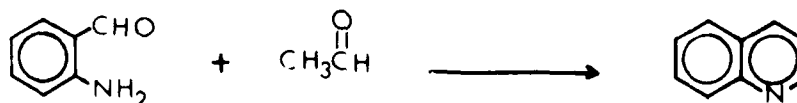
^a [Monomer] = 0.4 molar; solvent-NMP/Py=20/20 (v/v) for all experiments, except with p-aminobenzoic acid, for which 40/10 was used; temperature=2 hr at 80°C and 4 hr at 100-105°C; monomer/PCl₃/phenol=1 mole/1 mole/3 mole + 6% excess 4 wt % LiCl added.

^b H₂SO₄ at 25°C.

POLYQUINOLINES

Background

The Friedländer reaction,⁴³ is a base catalyzed condensation of an aromatic o-amino aldehyde or ketone with a ketomethylene compound. For example the reaction of o-aminobenzaldehyde with acetaldehyde affords a high yield quinoline. This reaction has been utilized, in fact to obtain aromatic



polymers.⁴⁴ The base catalyzed reaction of a bis-*o*-aminoaldehyde and a series of bisacetylaromatics yielded a series of low molecular weight polyanthrazolines. Although these polymers showed good thermal stability, they were low molecular weight materials and were soluble only in strong acids.

In our early work in these polymerization reactions, three important facts concerning the polymerization reaction and the polymers emerged:^{10,13,45,46}

1. The aldehyde function of the aminoaldehyde was not suitable, since it underwent side reactions and high molecular weight polymers were not obtained. Aryl ketone groups in place of the aldehyde gave high molecular weight materials.
2. Base catalysis was not suitable, but high molecular weight polymers could be obtained by acid catalysis.
3. Phenyl substitution on the polyanthrazolines, polyisoanthrazolines and polyquinolines greatly improved the solubility of these materials, and the phenyl group was conveniently introduced through the *o*-benzoyl group in place of the aldehyde moiety.

The phenylated polyanthrazolines and polyisoanthrazolines that were synthesized had high Tg's and Tm's, but were very difficultly soluble in common organic solvents.⁴⁶ A much more interesting class of materials, the polyquinolines,⁴⁷⁻⁴⁹ could be obtained by the Friedländer reaction.

Monomer Syntheses²⁷⁻²⁹

Three quinoline-forming monomers have been inexpensively synthesized in high yields by relatively simple reaction pathways (Figures 2 and 3). In the reaction sequence, Figure 2, high yields are obtained in each step and monomer of high purity could be obtained by recrystallization. The cyclization reaction of phenylacetonitrile with a bisnitroaryl to yield a bisbenz-isoxazole followed by hydrogenation has proven to be a good method for the

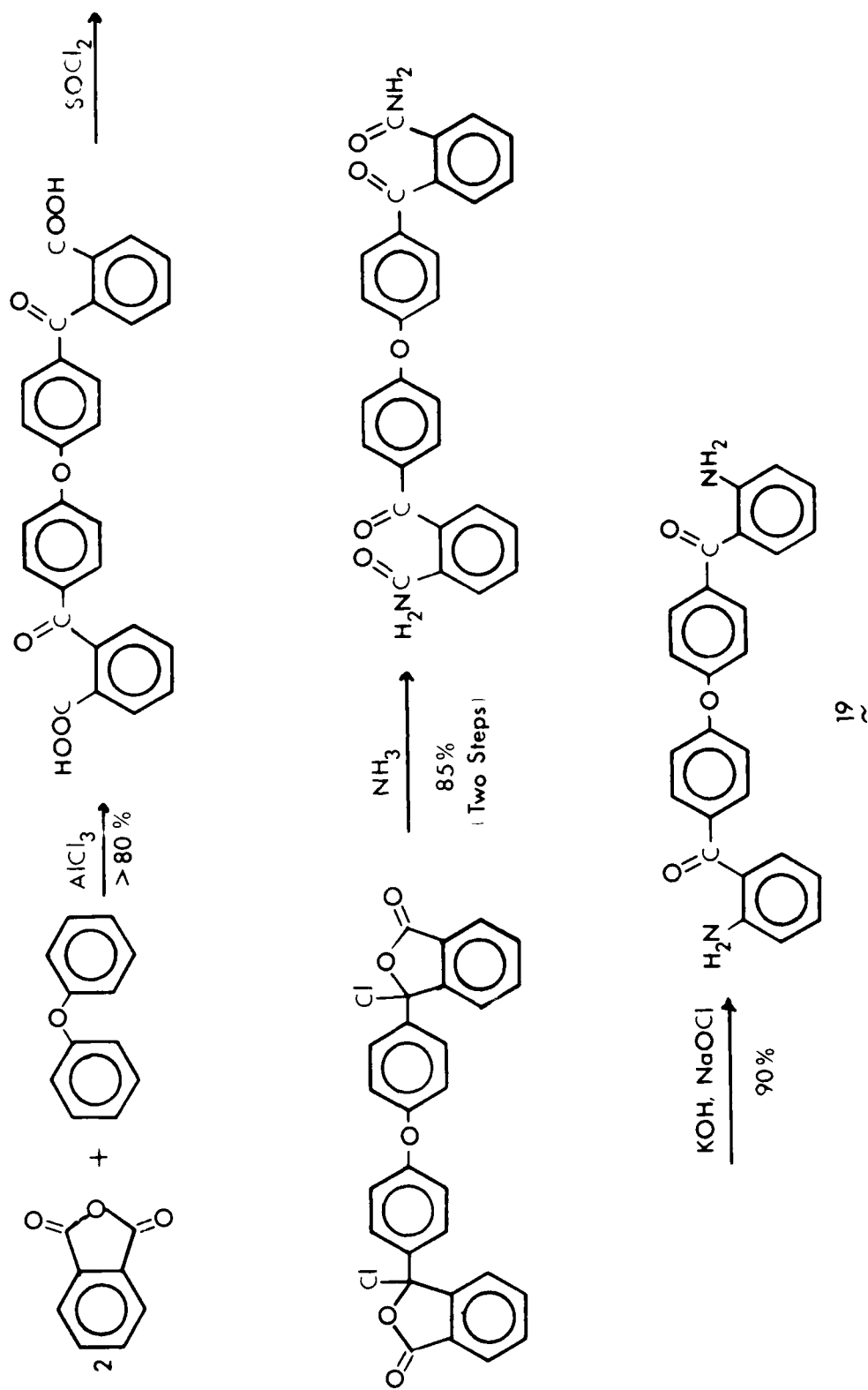


Figure 2
 Synthesis of 4,4'-Bis(2-aminobenzoyl)diphenyl Ether (19)

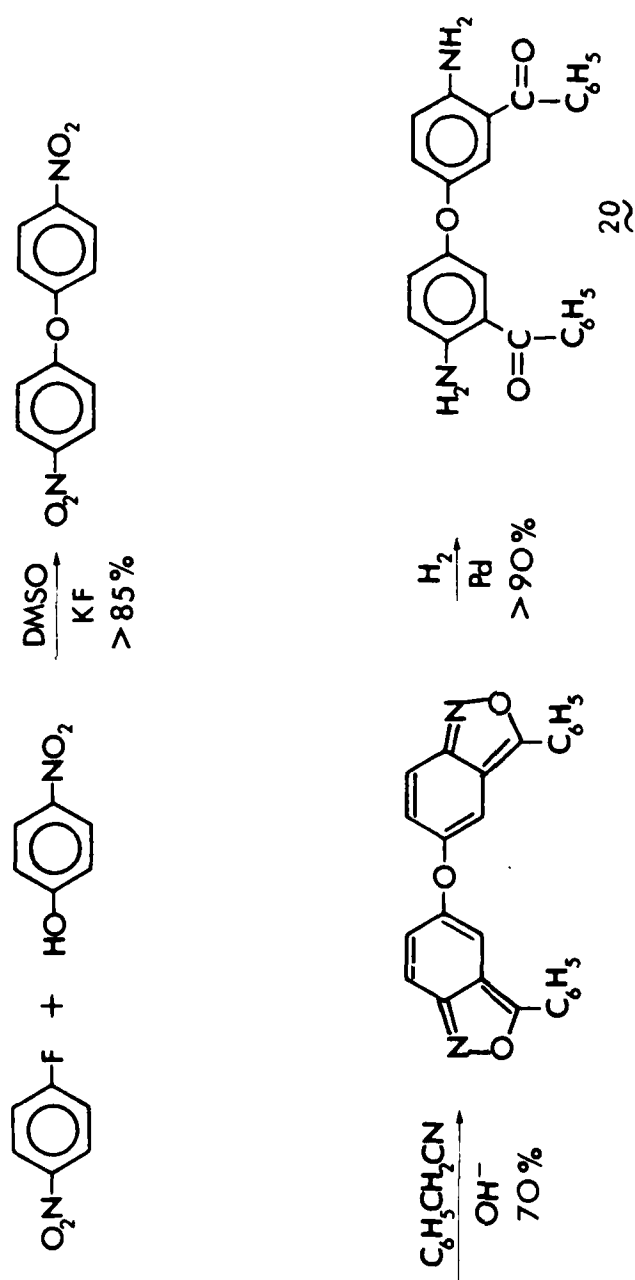
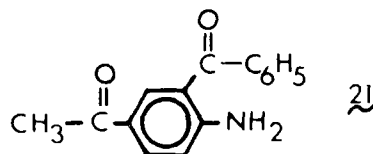


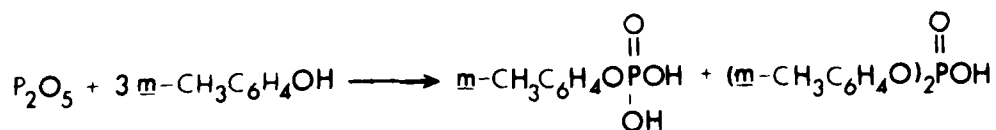
Figure 3
 Synthesis of 4,4'-Diamino-3,3'-dibenzoyldiphenyl Ether (20)

synthesis of 20 (Figure 3). An A-B monomer, 21⁵⁰ also has been synthesized by similar reaction sequence. A large number of diacetyl and diphenylacetyl monomers are either available commercially or are described in the literature.

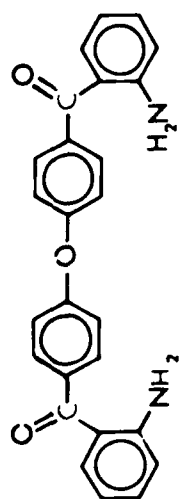


Polymerization Reactions^{48,49}

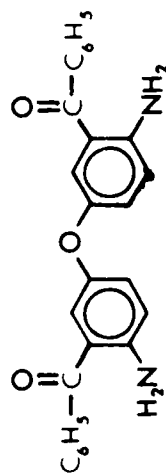
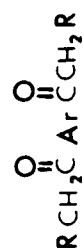
Representative polymerization reactions of the bisaminobenzoylaryl monomers (19 and 20) with the diacetyl and diphenylacetyl monomers (22 and 23) to give polymers containing quinoline units in the main chain are shown in Figure 4; the homopolymerization of the A-B monomer also is shown. Optimum polymerization rates and molecular weights were obtained initially either in mixtures of m-cresol and polyphosphoric acid or m-cresol and the reaction product of m-cresol and phosphorous pentoxide.^{48,49} The reaction product was shown by ³¹P nmr to consist of an equimolar mixture of the mono- and di-m-cresol esters of phosphoric acid, as the stoichiometry suggests.



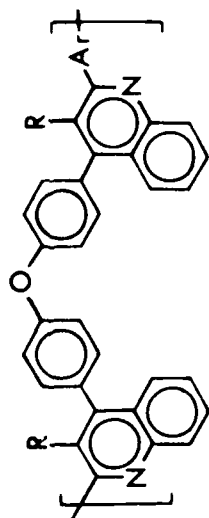
Both esters were independently synthesized, and although mixtures of the monoester and m-cresol were marginally effective as a polymerization medium, the diester with m-cresol effected the polymerization at about the same rate as the m-cresol phosphorous pentoxide reaction mixture (Fig 5). One added advantage of the independently synthesized (and purified) diester was that much higher molecular weights could be obtained. The upper degree of polymerization attainable in the phosphorous pentoxide m-cresol reaction mixture appears to be 320, possibly as a result of some side reaction with one or more of the monomer functional groups. Acid catalyzed cyclotrimerization has been



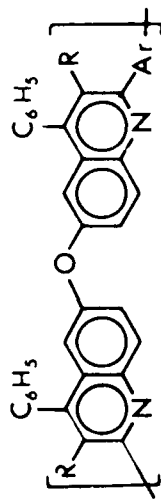
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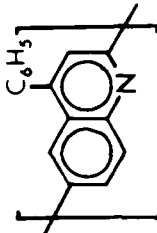
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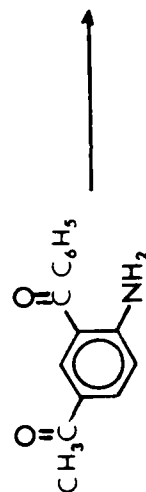
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Figure 4
POLYMERIZATION REACTIONS

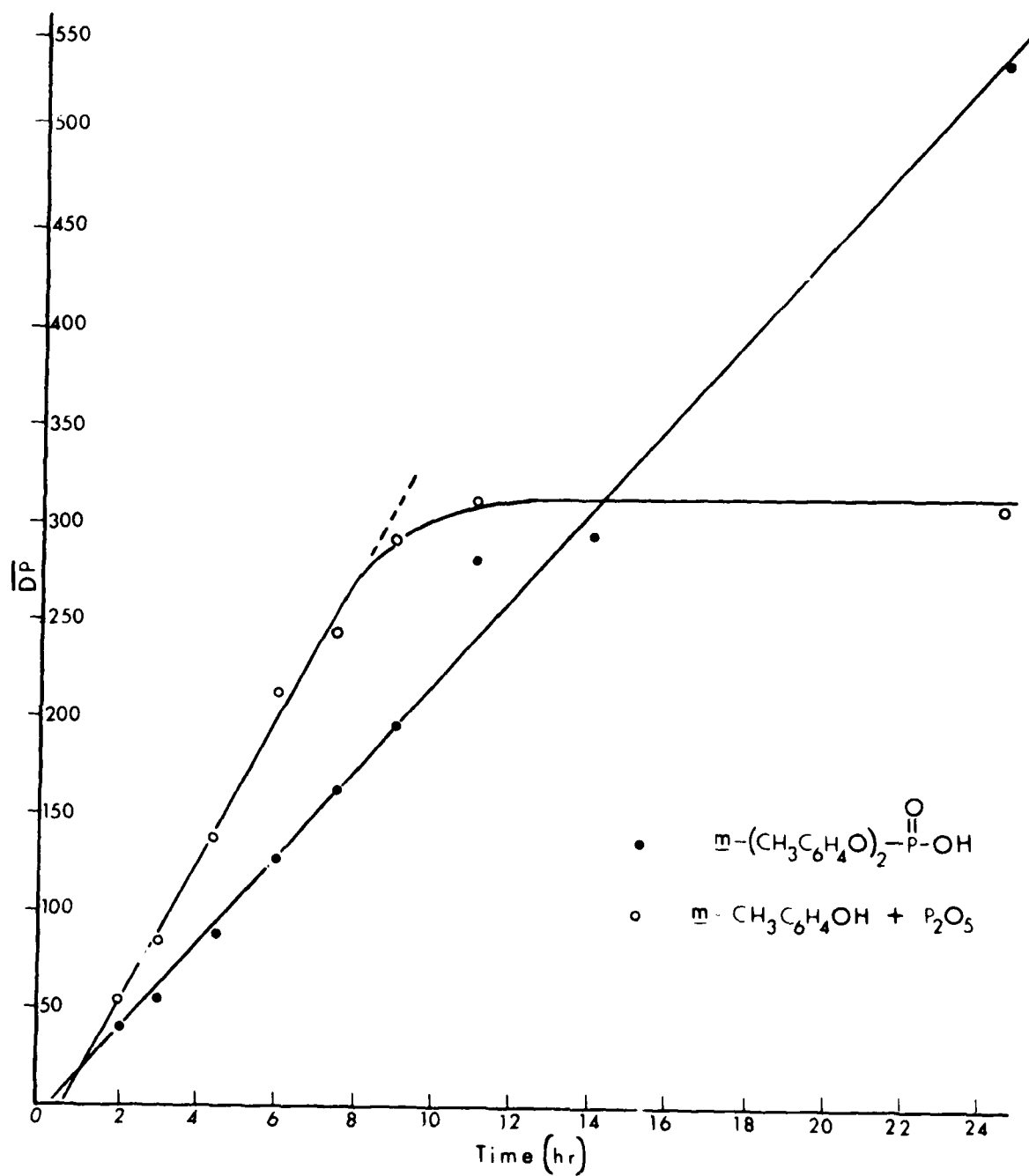


Figure 5

Kinetics of Polymerization of
20 With 4,4'-Diacetyldiphenyl
 Ether, 22 (Ar = 4,4'-C₆H₄OC₆H₄)

suggested⁴⁹ as a reaction which would not only consume ketomethylene groups but also would lead to branching. Thus, number average molecular weights in excess of 300,000 can be obtained, corresponding to an extent of reaction of ~99.9%.

Solution Properties

Polyquinolines are soluble in acidic solvents such as m-cresol, polar solvents such as N-methylpyrrolidone, and chlorinated hydrocarbons such as tetrachloroethane and chloroform, although the highly phenylated ($R = C_6H_5$) polymers tended to crystallize from chloroform on prolonged standing. Clear tough, flexible films could be cast from 15-30 weight percent solutions of the polymers, and fibers can be wet spun from these solutions. Surprisingly, the Mark-Houwink relationship obtained on fractionated samples of polymer 24, ($R = H$, $Ar = 4,4'$ -diphenyl ether) from osmotic pressure and viscosity measurements in chloroform showed a value of α of approximately 0.5,⁴⁸ indicating the ability of the chain to take a tighter coil in solution than might have been predicted.⁵¹ Under these conditions ($CHCl_3$, 20°C) the low second virial coefficient (7×10^{-7} cc-mole/gram²) and Huggins constant of 0.6 indicate a random flight configuration. Similar studies on polymer 25 ($R = H$, $Ar = 4,4'$ -diphenyl ether) revealed a larger value of α , 0.66.

For rod-like polyamides that form liquid crystalline solutions, unusually high molecular weight values obtained by light scattering have been reported⁵² that have been attributed⁵³ to association of the polymers in the amide solvent. Our low α values could be due to association at the concentrations of the chloroform solutions used for measurement. However, it has been shown⁵³ that in the case of poly(1,4-benzamide) α is 1.7 in the molecular weight range below 12,000, but at molecular weights above this, α is about 1, indicating that the chains are bending.

Gel permeation chromatography of polymer 25 ($R = H$, $Ar = 4,4'$ -diphenyl ether) provided a number average molecular weight (\bar{M}_n) of 51,600 and weight average molecular weight (\bar{M}_w) of 193,000 (based on polystyrene standards), in reasonable agreement with the \bar{M}_n value of 40,500 calculated by the Mark-Houwink equation for the sample. The dispersity of this polymer sample (\bar{M}_w/\bar{M}_n) is 3.75.

Polymer 26, obtained from the A-B monomer, 21 was soluble only in strong acids, but could be wet spun directly from the polymerization solution into methanol.

Phase Transition Temperatures, Thermal Stability and Thermomechanical Properties.^{54,55}

The thermal behavior of the polyquinolines is strongly affected by the thermal history. The polymers are composed not only of two phases, one crystalline, the other noncrystalline, but also within the noncrystalline phase there apparently exists multiple subphases, which in their glass transition interval, exhibit distinct first order transition behavior. All the polyquinolines, with one exception, exhibit a rather low degree (<20%) of crystallinity; polyquinoline 26 from the A-B monomer shows the highest degree of crystallinity (~60%). Preliminary X-ray data⁺ show the correct repeat distance for the recurring unit, but fiber samples of higher crystallinity will have to be obtained before a complete analysis can be done. Formation of the subphases in these polymers has been observed in the solid state, even under ambient conditions several hundreds of degrees below their glass transition temperatures.

The transition temperatures of this class of polymers (Table 8) met the requirements for melt processability in which the polymer is fabricated in the amorphous state above its glass transition temperature (250-350°C) and then annealed to develop crystallinity and raise the use temperature ($T_m \approx 450-550^\circ\text{C}$) to the limit of thermal performance as defined by the onset of thermal decomposition (TGA 520-580°C). Unfortunately, a high degree of crystallinity

⁺ Thanks to Professor J. Lando, Case Western University.

Table 8

Thermal Properties of Polyanthrazolines,
Polyisanthrazolines and Polyquinolines

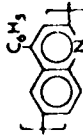
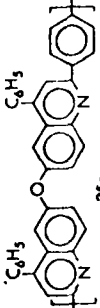
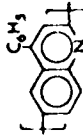
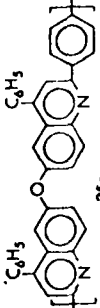
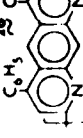
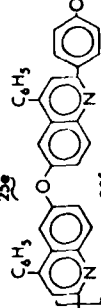
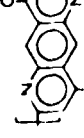
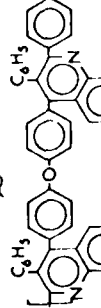
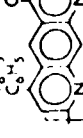
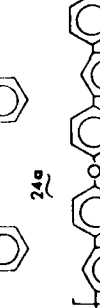
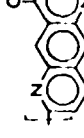
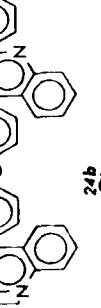
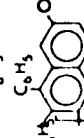
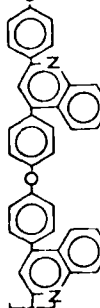
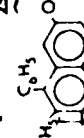
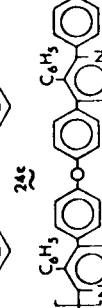
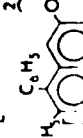
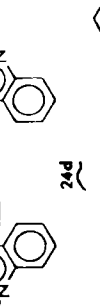
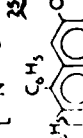
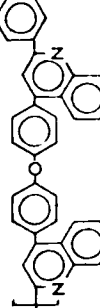
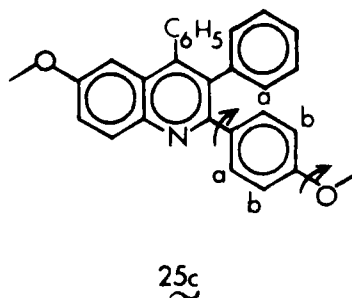
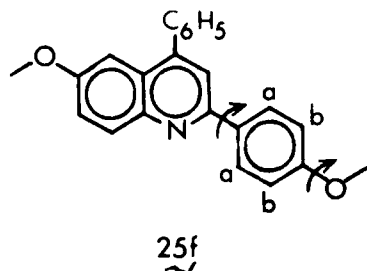
	η_{inh}	T_g °C	T_m °C	T_g/T_m	T_D °C	$(\Delta C_p)_{T_g}$ cal/mole ^c		η_{inh}	T_g °C	T_m °C	T_g/T_m	T_D °C	$(\Delta C_p)_{T_g}$ cal/mole ^c
	2.2	415	552	0.83	580	-		1.10	300	455	0.79	-	3.85
	0.62	392	513	0.85	580	3.90		1.80	266	448	0.75	-	3.00
	0.89	383	498	0.85	580	4.15		0.57	345	500	0.80	540	4.10
	0.77	379	502	0.84	540	3.60		0.38	326	475	0.80	575	-
	0.59	362	490	0.83	540	3.80		0.62	276	483	0.73	565	4.95
	4.10	351	480	0.83	-	5.10		0.26	273	AMORPH	-	520	-
	3.40	345	475	0.82	-	6.0		0.36	268	AMORPH	-	520	-
	2.00	305	476	0.77	-	5.20							
	3.10	308	480	0.77	-	4.00							

Table 8 (con't)

is not developed in these more flexible phenyl substituted polyquinolines.

The greater the chain rigidity, the higher the glass transition temperature. The difference between the glass transition temperatures ($\Delta T_g = 42 \pm 3^\circ\text{C}$) of the series of the more heavily substituted polyquinolines (5a-c) and those in which the 3-phenyl substitution is absent (5d-f) was attributed⁵⁵ to restricted rotation in the chain. In particular, substitution of phenyl for hydrogen should hinder rotation of the 2-phenylene unit.

Carbon-13 spin-lattice relaxation mechanisms are generally dominated by dipole-dipole interaction with neighboring nuclei, modulated by molecular motion. Because carbon atoms a and especially b in 25c and 25f have identical near neighbors, spin lattice relaxation time (T_1) can be related to molecular motion and thus chain mobility in solution. T_1 measurements on solutions of polyquinolines 25c and 25f by the inversion recovery method, 180° - t - 90° pulse sequence, show a greater chain mobility for 25f and 25c in agreement with the higher T_g for 25c in the solid.⁵⁶



The effect of structure on the melting points was less pronounced; the relative constancy of the T_m of structurally different polyquinolines, with the exception of polymer 26, is probably due to their low degree of crystallinity and crystal perfection.

The polyquinolines showed outstanding thermal stability in an inert atmosphere as well as in air. Generally, isothermal ageing of the polyquinolines showed no weight loss in air after 100 hr at 300°C . This excellent stability

is not surprising, since quinoline itself has been reported⁵⁷ to have the highest decomposition temperature of any of the aromatic rings.

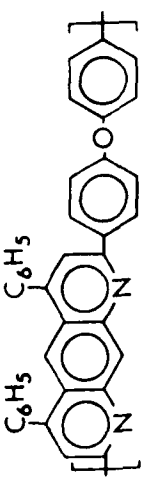
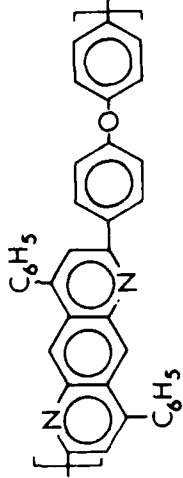
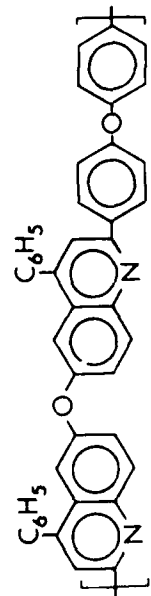
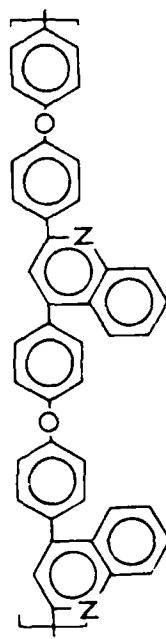
Under mild tensile stresses required for dynamic mechanical testing (Fig 6) the mechanical performance of films is as expected relatively constant up to the glass transition temperature. Above T_g mechanical losses become pronounced as shown by a drop in Young's modulus from $2-5 \times 10^{10}$ to less than 10^7 dynes/cm². This behavior is typical for noncrystalline, linear high polymers. Mechanical losses of low amplitude are observed in polyquinolines between 100° and 150°C. Since the decomposition temperature of 24c was above 510°C and the Young's modulus decreased from 2×10^{10} to 10^7 above T_g, melt extrusion through a large bore capillary at 430°C to afford a fiber with a diameter of 1 mm was possible. Stability of the material toward crosslinking under the extrusion conditions was indicated by retention of chloroform solubility. Due to a high melt viscosity, extrusion of fibers of finer denier was not possible. This fiber was then drawn at 270-280°C under mild tension, and the X-ray diffraction patterns of the stretched and unstretched polymer fibers showed an increase in crystallinity after drawing. Young's modulus (Table 9) decreases from 4.8×10^{10} dynes/cm² for the more rigid polyanthrazoline polymer to 1.9×10^{10} dynes/cm² for polymer 25f which contains an additional flexibilizing diphenyl ether linkage between the quinoline groups. The effect of annealing films above T_g on Young's modulus was shown for polymer 25f (Table 9). A film sample which was annealed at 280° for 2 hr followed by cooling at a rate of 0.5°C/min had a Young's modulus of 6.1×10^{10} dynes/cm² as compared to a value of 2.3×10^{10} for the original film sample.

In a preliminary run, polyquinoline 25f was spun from a NMP dope containing 12% solids at 150°C into concurrent nitrogen at 240°C.⁺ The relatively

⁺ Courtesy Dr. J.J. Kleinshuster and R.S. Irwin, Pioneering Research, Du Pont.

Table 9

Thermomechanical Properties of Polyquinolines

	[η]	T _g °C	T _{E'' max} °C	E' 25°C dynes/cm ²	E' above T _g
	0.51	379	382	4.8×10^{10}	7.2×10^7
	0.53	362	368	3.5×10^{10}	2.4×10^7
	0.94	266	271	2.3×10^{10} (6.1×10^{10})	2.4×10^7 9.0×10^7 **) **
	0.62	276	300	1.9×10^{10}	1.1×10^7

*Applied frequency = 35 Hz.

**Annealed above T_g (280°C for 2 hrs followed by cooling at a rate of 0.5 /min)

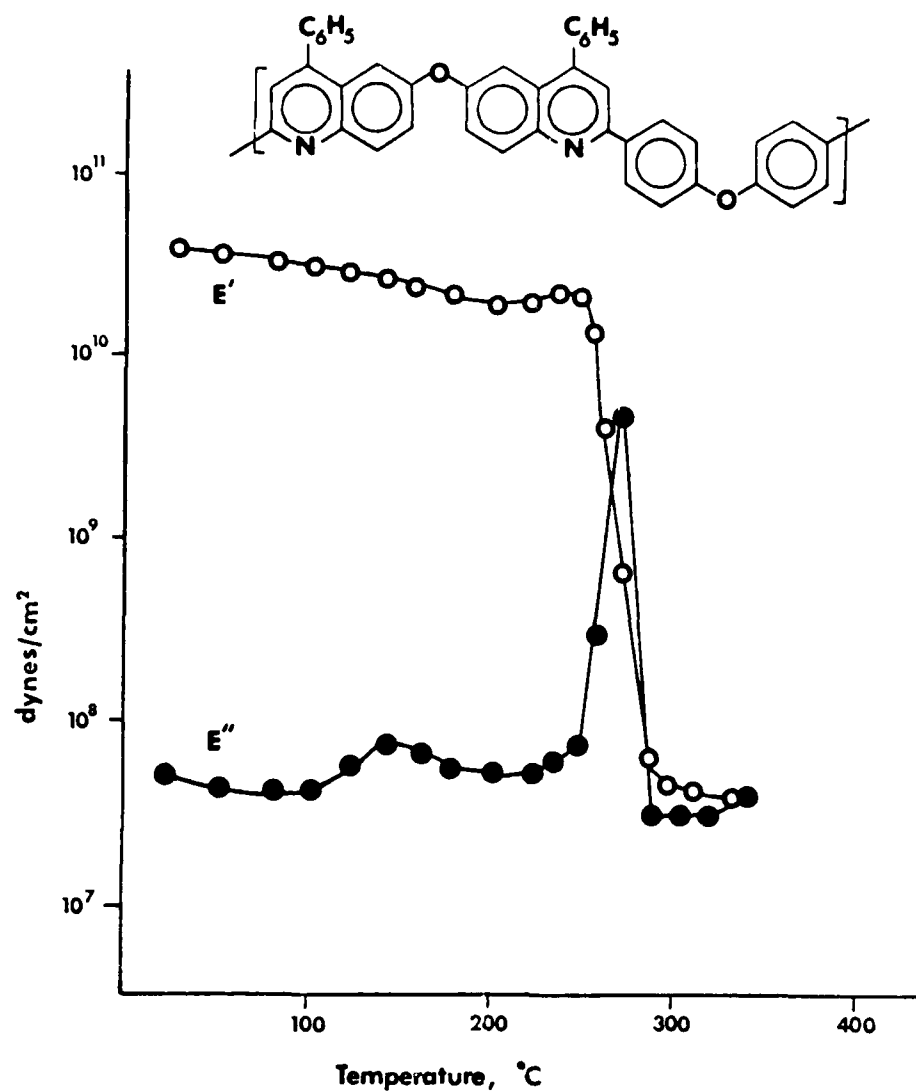


Figure 6
Dynamic Storage and Loss Modulus vs Temperature
Heating rate 5°/min, Atm He, Frequency 35 Hz

low percent elongation did not allow draw ratios greater than about 2, and a drawn fiber, unfortunately, did not show appreciable crystallinity. Tensile strength and moduli of only 3 gpd and 45 gpd, respectively, were obtained, but optimum spinning and drawing conditions were not attained. As indicated (Fig 6) an oriented film of 25f from chloroform has high modulus, modest tensile strength and low elongation combined with good dielectric properties (Table 10). Gas and water vapor permeabilities are relatively high. The thermal stability is excellent. A life in air of about 10 years at 200°C can be obtained by extrapolation of the Arrhenius data for isothermal aging. These times represent film failure, and are exceptionally good.

CROSSLINKING POLYPHENYLENES AND POLYQUINOLINES

Introduction

The major structural modifications of the polyphenylenes and polyquinolines that improve their solubility and processability are the addition of pendant phenyl groups and the introduction of flexible linkages, such as ether, or meta-phenylene groups, into the polymer backbone. In general, these structural modifications give the polymer a relatively low softening temperature which aids in fabrication; however, these modifications restrict the structural temperature to a value well below the thermal capabilities of the system.

The second approach to the synthesis of polymers that can be melt processed at relatively low temperatures requires a non-crystalline material with a low T_g that can be thermally cross-linked after or during fabrication to provide a use temperature that is limited only by the thermal decomposition temperature. The cross-linking reaction can be effected through the synthesis of monomers which incorporate the reactive site into the backbone of the polymeric heterocyclic polymer. After or during fabrication, the reactive function can be thermally induced to provide stable cross-links. Alternatively an

TABLE 10
 PROPERTIES OF UNORIENTED FILM SAMPLE
 OF POLYQUINOLINE 25f⁺

Thickness (mil)	0.3 - 0.4
η_{inh} (0.5% CHCl ₃ , 30°C)	1.59
Density (g/cc)	1.174
X-ray	Amorphous
T _g (°C)	266
<u>Electrical</u>	
Dielectric Strength (Kv/mil)	7.8
Volume Resistivity (ohm-cm/mil)	2.5×10^{15}
Dielectric Constant	2.6/2.5 (10 ² /10 ⁵ Hz)
Dissipation Factor	0.017/0.005 (10 ² /10 ⁵ Hz)
<u>Thermal Stability</u>	
TGA (5% wt. loss)	525°C (air) 630°C (N ₂)
Film Failure (Air aging)	2 hrs at 450°C 20 hrs at 350°C 11 days at 300°C 6 months at 250°C >10 years at 200°C*
*Extrapolated from Arrhenius-type plot	
<u>Permeability</u>	
O ₂ (cc/100 in ² - 24 hr - atm per mil)	2.78
Water Vapor (g/100 in ² - 24 hr - 44 mm per mil)	9.4

⁺ Courtesy Dr. R. Angelo, Plastic Products Department, Du Pont

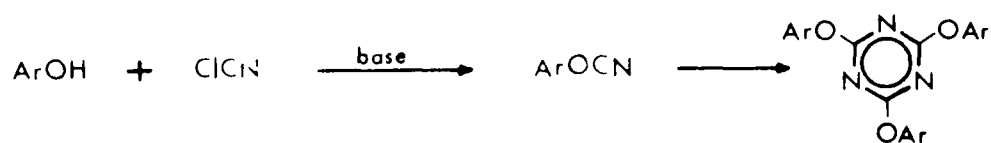
additive can be dispersed in the polymer at some stage before processing and then thermally processed to cross-link the fabricated polymer. The ideal additive should meet the following requirements: 1) Produce a reactive intermediate between 250-400°C or lower. 2) Produce a reactive intermediate that will react with aromatic nuclei such that a thermally stable cross-link will be formed. 3) Produce a reactive intermediate without excessive generation of highly volatile materials. 4) Have a high enough molecular weight such that it, its fragments or by-products will not come out of the polymer throughout the curing process. 5) Be compatible with the polymer such that it will be molecularly dispersed throughout. 6) Have some solubility in common organic solvents and be stable enough at room temperature to be shipped and handled safely.

When the cross-linking agent is incorporated into the polymer backbone, only requirement 1-3 must be met. If only a small percentage of the cross-linking agent is needed (<5%), the generation of a gas or other highly volatile materials may be tolerated provided bubbles or voids are not formed.

Aryl Cyanate Cyclotrimerization

One class of reactions that meets all these requirements is the cyclic trimerization reaction of triply bonded atoms.

One of the most reactive classes of compounds with respect to the cyclic trimerization is the aryl cyanates. Quantitative yields of trisaryls-triazines (aryl cyanurates) have been obtained from the cyclotrimerization of aryl cyanate.⁵⁸⁻⁶⁰ The reaction is promoted by heat, protonic acids, Lewis acids, and bases,^{58,61,62} and can be carried out in a number of solvents or neat.⁶² The trimerization of cyanates is highly selective when compared to other cyclotrimerization reactions in which chain polymerization and dimerization



compete as side reactions.⁶² Phenyl cyanurate has been reported^{63,64} to be relatively chemically inert. The cyanate cyclotrimerization reaction has been employed as a polymer forming reaction^{65,66} and a crosslinking reaction for polyquinoxalines.⁶⁷

Fiberglass laminates prepared using the biscyanate derived from bisphenol-A show high thermostability including good mechanical properties and excellent electrical resistance at elevated temperatures, as well as excellent chemical resistance.⁶⁸

The applicability of cross-linking by aryl cyanate cyclotrimerization to a wide variety of thermally stable polymers was carried out by the synthesis and subsequent crosslinking of phenylated polyphenylene and polyphenylquinoxaline prepolymers.⁶⁹ The only restriction placed upon the type of polymer system that may be utilized is the ease with which hydroxyl groups, which are converted to the cyanate moiety, can be incorporated into the appropriate prepolymer.

The addition of a monofunctional acetylene, *m*-hydroxyethynylbenzene to the polymerization reaction of *p*-diethynylbenzene and the oxybistetracyclone served to limit the average molecular weight of the polymer by terminating the growing chains with an aryl hydroxyl group (Figure 7). The phenolic groups were converted to cyanate ends by reaction with excess cyanogen bromide in the presence of triethylamine.

The synthesis of polyphenylquinolines by the condensation of 4,4'-diacetyldiphenyl ether with 4,4'-diamino-3,3'-dibenzoyldiphenyl ether is readily adapted to the synthesis of hydroxyl end-capped prepolymers by the

addition of p-hydroxyacetophenone to the polymerization reaction. Two bis-hydroxy prepolymers with a relatively short chain length were prepared and converted to the biscyanato phenylquinoline prepolymers by treatment with excess cyanogen bromide in chloroform solution (Figure 8).

Different glass transition temperatures were observed for the cyanate end-capped prepolymers, depending on the molecular weights. (Figure 7 and 8) The temperature at which the cyclotrimerization took place (exotherm) increased with increasing molecular weight, suggesting that shorter polymer chains were more mobile and contained a higher relative concentration of cyanate ends, thus increasing the probability of a termolecular collision. The maximum in the exotherms ranged from 270-400°, but curing could be effected at lower temperatures. Cyclotrimerization did not take place below the T_g of any given sample. Generally the reaction could be carried out at 250-300° for 0.5-1 hr; lower temperatures required longer reaction times. Films of the higher molecular weight polyquinoline could be cured to afford a tough, transparent yellow film.

The cured polymers showed an increase of the apparent T_g over those of the corresponding biscyanato prepolymers. These values of T_g did not exceed those of the parent polymers because of the copolymer effect⁷⁰ induced by the presence of the cyanurate structures. These materials were insoluble and showed thermal stabilities characteristic of the parent polymer systems, although initial weight losses of 4-8% above 400° were shown to be caused by the loss of cyanuric acid from the cross-linking sites. Hydrolytic stability of these materials were very good in acidic or basic aqueous media, but complete degradation of the cross-linking structures occurred in a strongly basic, swelling solvent medium.

Thus, although the cyanate group provides an effective reaction site for

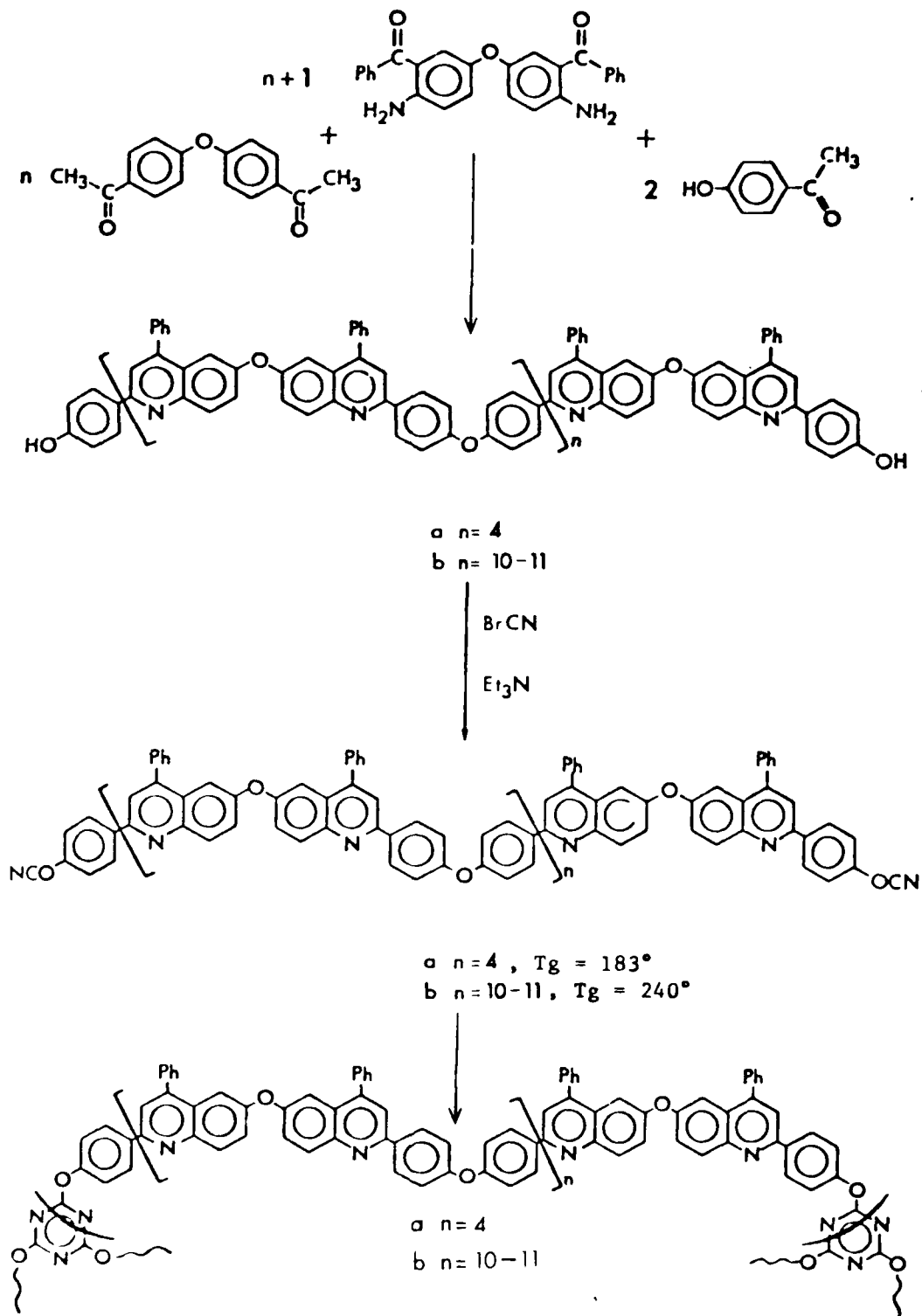


Figure 8
Cyanate Crosslinking of Polyquinolines

cross-linking, the product cyanurate is not as thermally stable as the parent polymers, it hydrolyzes in a solvent that is a good solvent for the parent polymer and therefore will swell the resin, and it tends to lower the apparent Tg as a result of the copolymer effect. Measurements to examine the flow characteristics of these polymers under load at elevated temperatures were not made.

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